“The mechanisms by which the Marcellus gas shale sequesters residual treatment water (RTW)”

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\body The international rush to produce gas within shale by horizontal drilling and massive slickwater hydraulic fracturing (i.e., fracking) has prompted concerns that fracking may harm global health (1). Concerns involving water quality arise because as much as 2 x 10^4 m^3 of water-based fluid is injected into gas shale to open fractures near each horizontal well (Table 1). Prior to injection, water is treated to prevent bacterial growth, to prevent scaling of steel pipes, to aid in rapid flow, to prevent swelling of the clay minerals in the shale, and to carry sand which props fractures open. Once fractures within the gas shale are opened, the treatment water reacts with constituents of the shale to gather up salt, some metals, and a few radionuclides. During the lifetime of a gas-shale well less than half of the treatment water is recovered as flowback or later production brine (2). While recovered treatment water is easily managed, residual treatment water (RTW) slips beyond the control of engineers. Presently, the fate of this RTW, more than 10^4 m^3 per horizontal well, is uncertain. The question is whether the RTW might someday appear in groundwater (3).

The report by Warner *et al.* in this issue of PNAS (3) focuses on the migration of natural brine as a proxy for migration of RTW. Warner *et al.* conclude that the Type D waters mark cross formational pathways where high Br/Cl, low $^{87}Sr/^{86}Sr$, high Sr/Ca brines have migrated from the deep formations in the past. They do not state when this cross formation brine migration took place, but imply (by mentioning it’s methane richness and it’s prevalence in valleys where present-day escape is more likely because of a freshwater sweep from highland infiltration) that the natural migration is ongoing today. By referring to the source repeatedly as the “Marcellus” they suggest that leakage is from the Marcellus. They suggest the pathways of natural gas leakage might be areas of higher risk for leakage of RTW. The implication is that the Marcellus is leaking now, naturally without any human assistance, and that if water-based fluid is injected into these cross-formational pathways, that leakage, which is already ‘contaminating’ the aquifers with salt, could be made much worse.

In the Appalachian Basin high Br/Cl brines are residuals from extensive evaporation and halite precipitation of seawater (4). **One of two** geologically reasonable **sources** is residual pore fluids in the Silurian Salina salt. These residual brines were almost certainly squeezed out by salt deformation during the Alleghanian orogeny some 270-260 million years ago (5). These brines likely contaminated the Marcellus and the Upper Devonian section at that time by mixing into a deep regional flow system originating in the high Alleghanian uplands to the SE.

Using a typical electric log from the Marcellus, it is clear that the volume of free water within the Marcellus is so small it cannot support ongoing contamination of the shallow aquifers with high Br/Cl brine as observed by *Warner et al.* (3) even assuming it is leaking (Figure 1). If fully saturated and completely mixed into treatment water, the natural free water could bring the salinity of flowback up to ≈

10^5 ppm (Table 1). The volume of the capillary bound water is also more than sufficient to increase the salinity of the treatment water as observed. The Marcellus water chemistry reported in Warner *et al.* (3) is most likely found in treatment water salinized *in situ* and is, therefore to be distinguished from natural brines produced by oil and gas wells from the Medina, Tuscarora, and Oriskany sandstones (6).

The Marcellus has plenty of joints as a consequence of gas generation and expulsion (7). These joints have a very low innate water-filled ϕ largely because early gas became saturated in water and **the free water** was carried off during expulsion, leaving behind **stratabound** salt (**Blauch, 2009**). This process **progresses** to the point that **residual brine** in the Marcellus **evolved** beyond halite precipitation (Figure 1). Thus the Marcellus, and other gas-generating shales become relatively dry and the **residual brine** they contain will tend toward the high Br/Cl variety.

Why are the Marcellus and other gas shales such a good seals? The strata surrounding the Marcellus and similar gas filled shales contains water, and so capillary seals will form at their margins (8). These capillary seals form automatically in the presence of a porous media with variations in porosity and two fluids. They are virtually indestructible, and for this reason trap gas in basins virtually forever. In the case of the Marcellus they have trapped in the gas for at least 200 million years (this being the end of the period when it was generated).

Several observations serve as evidence that fluids are not leaking from the Marcellus today. The Marcellus is the seal over very large Oriskany gas fields in NY and PA holding an initial pressure head of > 0.7 psi.ft (9). Shut-in tests within the Marcellus show gas pressure > 0.85 psi/ft (proprietary). Joints containing water tend to heal in the form of veins. Common Marcellus joints are gas charged and unhealed (6). The Marcellus carries a low water saturation (< 10%). High gas pressure indicates that, even if fractures within the Marcellus are interconnected, they are sealed by a capillary-bound water. Yes, the gas in the Marcellus today is highly over pressured, but this does not mean gas is leaking out; it is firmly trapped by capillary seals. If it was leaking even a very very little, it would now be all gone. 200 million years (the end of active gas generation with the onset of exhumation) is a long time to leak.

There is no doubt that deep basin brine passed through the Marcellus during Alleghanian tectonics as witness by Marcellus veins with 26 wt % equivalent NaCl fluid inclusions (10). Certainly, it is reasonable to suppose that the free water in the Marcellus has the same salinity. The most likely place for deep basin brines to have passed through the Marcellus and its Upper Devonian overburden is in the more heavily fractured core of anticlines where more faults are found (11). However, many of these faults are low angle and likely to be smeared with clay fault gouge, a low permeability seal rock.

While 10^4 m^3 of RTW may seem like a large volume, the reservoir volume that is stimulated by hydraulic fracturing is much larger (Table 1). If imbibed pervasively in the stimulated reservoir volume, the RTW could be absorbed by a porosity (ϕ) of roughly 0.06%. Spontaneous imbibition is a form of wicking made possible by a high capillary pressure within the water-wet matrix of very fine grained rocks like gas shale. Imbibition is limited to a zone near fracture walls where water invasion can be 3 cm in an experimental time frame of three days in nanoDarcy permeability shales (2). If fracture spacing is as low as 1 m only 5 cm of matrix penetration by imbibition will sequester the entire charge of RTW in a shale ϕ of 0.6%. If RTW is caught in the tip regions of fractures, less imbibition is necessary for total sequestration. RTW

sequestered by a combination of imbibition and flow to joint-tip regions is of no further concern to global health particularly when mantled by a capillary seal (8).

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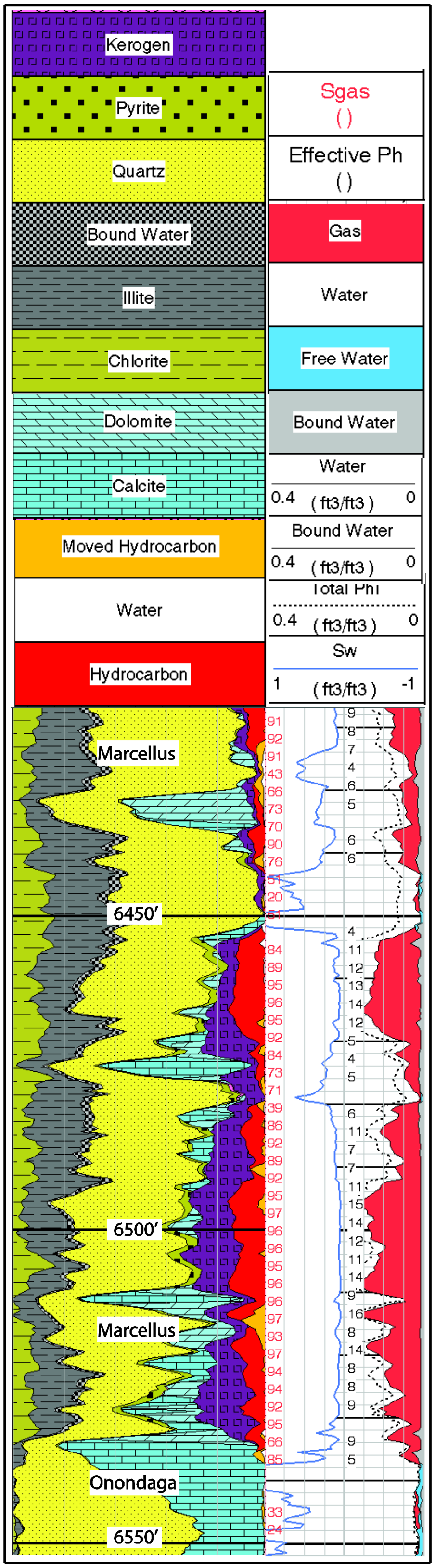
Figure 1. A proprietary Schlumberger ELAN (Elemental Log Analysis) showing that the Marcellus is a quartz/clay mudstone with limestone stringers (left tract). At 6505' kerogen and the gas filled porosity in the kerogen constitute 30% of the volume of the rock. Most of the water in the rock is clay-bound. The rest of the water in the Marcellus is either capillary-bound or free (left tract – white). Moved hydrocarbon is the volume of hydrocarbon per unit volume of rock that have been displaced by invasion of drilling mud (left tract - orange). Total porosity in the Marcellus (ϕ) includes 2% and 5% clay-bound water which does react with residual treatment water (right tract – white). The maximum effective ϕ at 15% in the Marcellus is gas charged and this ϕ is found in oil-wet kerogen where gas saturation approaches 100% (right tract – red). A much smaller fraction of the effective ϕ is water filled and only portion of the effective ϕ contains free water subject to Darcy flow (right tract – blue). Capillary-bound water is evenly distributed through the 150' section of the Marcellus (right tract – gray).

Table 1.

Volume of Marcellus tapped	$15.3x10^6$ m^3	=(83 acres)(4047 m^2/acre)(150 ft)(0.3048 m/ft)
Volume of treatment water	$2x10^4$ m^3	=5.3 million gallons
Volume of capillary-bound water	$1\text{-}2x10^5$ m^3	=(1% - 2% porosity)($15.3x10^6$ m^3)
Vol. of free water that could leak	8,160 m^3	=(8 ft/150 ft)(1% porosity)($15.3x10^6$ m^3)
Volume filled with gas	$1.2x10^6$ m^3	=(≈8% porosity)($15.3x10^6$ m^3)



Kerogen
Pyrite
Quartz
Bound Water
Illite
Chlorite
Dolomite
Calcite
Moved Hydrocarbon
Water
Hydrocarbon
Sgas
( )
Effective Ph
( )
Gas
Water
Free Water
Bound Water
Water
0.4 (ft3/ft3) 0
Bound Water
0.4 (ft3/ft3) 0
Total Phi
0.4 (ft3/ft3) 0
Sw
1 (ft3/ft3) -1
Marcellus
6450’
6500’
Marcellus
Onondaga
6550’